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(54) Title of the Invention:

PROCESS FOR THE FORMATION OF FOAMS FROM SYNTHETIC RESIN EMULSIONS

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## S P E C I F I C A T I O N

### 1. Title of the Invention

PROCESS FOR THE FORMATION OF FOAMS FROM SYNTHETIC RESIN EMULSIONS

### 2. Scope of the Patent Claim(s)

(1) Process for the formation of foams, characterized by the mechanical foaming of synthetic resin emulsions that contain at least one of a metaphosphate (I), polyphosphate (II), and ultraphosphate (III), with the following structural formulas, followed by coating them on substrates or pouring them into molds, with subsequent heat treatment.



in which **M** represents Na, K, and Ca, and **n** is a positive integer.



(2) Process for the formation of foams as described in Claim 1, characterized in that the synthetic resin emulsions are one of a polyurethane emulsion, a conjugated diene, and/or a vinyl polymer emulsion, or their mixtures.

### 3. Detailed Description of the Invention

#### Field of Industrial Application

The present invention pertains to a process for the formation of foams from synthetic resin emulsions. More precisely it pertains to a process for the stable formation of modified foams with high strength from synthetic resin emulsions selected from one or a suitable mixture of a polyurethane emulsion, a

conjugated diene, and/or a vinyl polymer emulsion that contain a specific phosphate.

### Conventional Techniques

The most common process up to now for the formation of foams consists in adding a foaming agent, a coagulating agent, a crosslinking agent, and other additives to a natural and synthetic resin emulsion, followed by mechanical foaming of the mixture, coating the mixture on a substrate or pouring it into a mold, then drying, coagulating, and curing to form a foam. Examples of a natural and synthetic resin emulsion of this kind include natural rubber latex, styrene-butadiene copolymer emulsion, acrylonitrile-butadiene copolymer emulsion, acrylic acid ester copolymer emulsion, etc. The foams formed in this way are then used for various purposes based on their structural advantages, such as lightness, thickness, tactility, etc.

However, many of these foams are inferior in mechanical strength and durability, and if they are to be used for multiple purposes, their mechanical strength and durability have to be improved. For example, in the case of natural rubber and butadiene copolymer, the durability with regard to resistance to light and heat must be improved and the mechanical strength must be improved as well. In the case of acrylic acid ester copolymer, the mechanical strength, solvent resistance, cold resistance or elasticity, etc., must all be improved.

On the other hand, various processes for the formation of foams from polyurethane have been proposed, and because these foams turned out to be high-performance foams after the above-mentioned drawbacks were eliminated, they have been attracting considerable attention. However, when the conventional mechanical foaming process was used for polyurethane emulsions, the foamability was not satisfactory and the original characteristics of the resin were not utilized for developing multiple uses, thus an improvement was necessary. For example, stable and wide-range foamability, which can lead to foams with a high expansion ratio and thick coating, is lacking, thus an improvement is needed.

Thus, in the formation of foams from synthetic resin emulsions, excellent foam properties with high strength and durability are being demanded and at the same time it must be possible to form the foams into industrially useful shapes in a stable manner. However, none of these goals has been realized.

### Problems to be Solved by the Invention

In conventional technology, it is foamability that is important and yet poses the most difficult problems. For

example, the bubbling of an emulsion is to form bubbles in a uniform manner and maintain them, and to form a resin film with strength enough to durably maintain the bubbles without their coalescing or becoming extinct from an aqueous dispersion, which is an emulsion essentially with no strength which forms and air bubble-containing partition (wall). Namely, there is a need for mutually opposite properties, that is, the dispersion stabilization capability of the emulsion and also the dispersion instabilization capability with regard to the rapid merging of dispersed resin particles. Therefore the improvement of physical properties by the joint use of different types of emulsions adopted in a nonfoaming system is difficult in a foaming system due to difference in the dispersion stabilization capability and dispersion instabilization capability of the emulsion. In fact, a mixed emulsion consisting of polyurethane emulsion and styrene-butadiene copolymer emulsion prepared using conventional techniques will either become much thicker during mechanical foaming and coagulate to end up looking like bean curd (tofu), or the resulting foam will contain many large air bubbles.

Consequently, these mixtures have no commercial value. A mixture of polyurethane emulsion and acrylic acid ester copolymer emulsion behaves in a similar way. For example, at the time of forming with a high expansion ratio and coating thickness, because of an increase in the size of the air bubbles and extinction of the air bubbles, these mixtures have relatively little commercial value. In the case where the amount of one of the emulsions is kept very small, and in the case of same-system emulsions or with a low expansion ratio and thin coating (e.g., about 1 mm thick), it is not impossible to obtain products with some commercial value, however, we were unable to improve both the physical properties of the foams and foamability, thus we were unable to satisfy the above-mentioned requirements.

The object of the present invention is to solve the above-mentioned problems.

#### Means for Solving the Problems

The present inventors carried out an extensive study on the foamability of foams from synthetic resin emulsions with remarkably improved strength, durability, and foamability which enabled us to conduct stable foaming into industrially useful forms. As a result, it was found that when synthetic resin emulsions were used in the presence of specific substances, it was possible to impart excellent foamability as well as excellent physical properties to the foams. It was this discovery that led to the development of the present invention.

Namely, the present invention provides a process for the formation of high-strength foams, characterized by the mechanical

foaming of synthetic resin emulsions, preferably either a single emulsion or a mixture selected from a polyurethane emulsion, a conjugated diene, and/or a vinyl polymer emulsion that contains at least one of a metaphosphate (I), polyphosphate (II), and ultraphosphate (III) with the structural formulas listed below, followed by coating them on substrates or pouring them into molds, with a subsequent heat treatment.

The object of the present invention is to provide foams with excellent mechanical strength, heat resistance, light resistance, chemical resistance, and elasticity. Another object is to provide emulsions with industrially useful foamability which can form such high-performance foams stably and in many different forms. Another object of the present invention is to provide a process for the formation of foams from a mixture of a polyurethane emulsion and another emulsion which is prepared entirely by the use of a different process.



in which **M** represents Na, K, and Ca, and **n** is a positive integer.



According to the present invention, to a synthetic resin emulsion that contains at least one of a metaphosphate (I), a polyphosphate (II), and ultraphosphate (III), if necessary, a foaming assistant, a viscosity adjusting agent, a foam controlling agent, a crosslinking agent, etc. may be added, then a gas (mainly air) is blown into the resulting mixture which is stirred to bring about foaming. Next, a substrate is coated with the foaming solution or the foaming solution is poured into a mold, followed by heat treatment, to obtain a uniformly porous foam with excellent surface smoothness as well as excellent mechanical strength and durability, even under conditions of a high expansion ratio, high-speed processing (high-speed discharge, coating, and drying using a continuous mechanical foaming machine), and thick coating.

The synthetic resin emulsion of the present invention is a single emulsion or a mixture of emulsions selected from polyolefins (polypropylene, polyethylene), fluoropolymers, polyacetals, phenolic resins, epoxy resins, alkyd resins, polyester resins, polyurethane, conjugated dienes, and/or vinyl polymers.

The polyurethane emulsions used in the present invention are already known and can be prepared by various processes. For example, it is suitable to use an emulsified polyurethane solution and also a polyurethane emulsion prepared by the reaction of a polyhydric compound with terminal hydroxyl groups with an organic polyisocyanate in an amount which is greater than

the stoichiometric amount, followed by emulsifying the prepolymer obtained in this way in an aqueous dispersion using a surfactant, then a chain extender is added to extend the length of the chain of the prepolymer, as described in Japanese Kokoku Patent No. 33[1958]-1,141.

The molecular weight of these polyhydric compounds is usually 300-4,000, and preferably 600-3,000, and typical examples include polyether polyol, polyester polyol, and polycarbonate polyol.

A polyether polyol can be prepared using at least one compound that has at least 2 active hydrogen atoms selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, trimethylene glycol, 1,3-butylene glycol, tetramethylene glycol, hexamethylene glycol, decamethylene glycol, glycerol, sorbitol, sucrose, aconitic acid, trimellitic acid, hemimellitic acid, phosphoric acid, ethylenediamine, propylenediamine, diethylenetriamine, triisopropanolamine, pyrogallol, dihydrobenzoic acid, hydroxyphthalic acid, 1,2,3-propanetriol, etc., as an initiator and then addition polymerization of at least one monomer selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, styrene oxide, epichlorohydrin, tetrahydrofuran, cyclohexylene, etc., using a common process.

On the other hand, a polyester polyol can be prepared by condensation polymerization of at least one compound having at least two hydroxyl groups selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, trimethylene glycol, 1,3-butylene glycol, tetramethylene glycol, hexamethylene glycol, decamethylene glycol, glycerol, trimethylolpropane, pentaerythritol, sorbitol, etc., with at least one compound having at least two carboxyl groups selected from the group consisting of malonic acid, maleic acid, succinic acid, adipic acid, tartaric acid, pimelic acid, sebacic acid, oxalic acid, phthalic acid, terephthalic acid, hexahydrophthalic acid, aconitic acid, trimellitic acid, hemimellitic acid, etc., using a common process.

A single compound can of course be used as the polyhydric compound, such as a polyether polyol or a polyester polyol, however, a mixture of at least two of them can also be used. And in addition, they can be mixed with a low-molecular-weight polyol and then used. Examples of suitable low-molecular-weight polyols include ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, trimethylene glycol, 1,3-butylene glycol, tetramethylene glycol, hexamethylene glycol, decamethylene glycol, glycerol, trimethylolpropane, pentaerythritol, sorbitol, etc.

Examples of suitable organopolyisocyanates include aliphatic, alicyclic, or aromatic polyisocyanates such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, m-phenylene diisocyanate, xylylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, lysine

diisocyanate, 1,4-cyclohexylene diisocyanate, 4,4'-dicyclohexyl diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 3,3-dimethoxy-

4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, 3,3'-dichloro-4,4'-biphenylene diisocyanate, 1,5-naphthalene diisocyanate, 1,5-tetrahydronaphthalene diisocyanate, biphenyl 2,4,4'-triisocyanate, etc.

The chain extenders are compounds with at least two active hydrogen atoms which can react with an isocyanate group.

Examples of suitable chain extenders include glycols such as ethylene glycol, tetramethylene glycol, hexamethylene glycol, diethylene glycol, monoethanolamine, ethylenediamine, triethyl-

enediamine, 1,2-propylenediamine, hexamethylenediamine, **N**-(hydroxyethyl)-

ethylenediamine, **N,N'**-[bis(2-hydroxyethyl)]ethylenediamine, **m**-phenylene-

diamine, 2,4-tolylendiamine, bis(4-aminophenylmethane), 3,3'-dichloro-4,4'-

diaminodiphenylmethane, piperazine, 2-methylpiperazine, etc.; alkanolamines; and diamines. However, the reaction product of 1 mole of an alkylendiamine with 2 moles of acrylamide and the reaction product of 1 mole of an alkylendiamine with 2 moles of acrylonitrile also can be used.

In the case of the present invention, there are no limitations with regard to the solids concentration of the polyurethane emulsion, however, from the standpoint of profitability at the time of drying and the homogeneity of the foam, it is suitably 30-60% by weight, and preferably 40-50% by weight.

The conjugated diene and/or vinyl polymer emulsions used in the present invention are prepared by the radical emulsion polymerization of at least one monomer selected from an ethenic unsaturated monomer and/or a conjugated diene monomer. This includes all of the conjugated diene and/or vinyl polymer emulsions for mechanical foaming in that technical field, such as emulsions of acrylic acid ester polymer, styrene-butadiene polymer, acrylonitrile-butadiene polymer, methyl methacrylate-butadiene polymer, vinyl acetate polymer, ethylene-vinyl acetate polymer, vinyl acetate polymer, etc. The solids concentration of these emulsions is 30-60% by weight, and preferably 40-50% by weight. Among these emulsions, emulsions of acrylonitrile-butadiene polymer, styrene-butadiene polymer, and acrylic acid ester polymer that contain carboxyl groups work especially well.

Examples of suitable conjugated dienes for use in the present invention include 1,3-butadiene, 2-methyl-1,3-butadiene, 2-chloro-1,3-butadiene, etc. However, considering profitability and copolymerizability with other monomers, the use of 1,3-butadiene is preferred.

The ethenic unsaturated monomers used in the present invention

**PAGE 63 (COLUMNS 15-18) OF THE ORIGINAL JAPANESE PATENT KOKAI IS MISSING.**

.... especially preferable. The concentration process is usually carried out at 50-70°C and a pressure of 500-600 mm Hg, however, this process is not restricted to these conditions.

The effect of the presence of phosphates (I)-(III), which characterizes the present invention, will now be explained. Phosphates (I)-(III) increase the mixing stability when polyurethane emulsions and conjugated diene and/or vinyl polymer emulsions, whose resin properties and aqueous dispersion form are different from those of the polyurethane emulsion, are used together.

In the synthetic resin emulsions of the present invention, due to the presence of the phosphates, the stability of the synthetic resin emulsions increases and stable compounding with various additives becomes possible, thus the functions of the additives can be thoroughly realized. For example, at the time of compounding a coloring agent, uniform coloration and quantitative coloration become possible, thus the commercial value can be increased. And the stability of the bubbling emulsion increases, therefore there is practically no extinction of the bubbles at the time of coating with the bubbling emulsion or at the time of pouring the bubbling emulsion into a mold. Moreover, at the time of formation of a foam by heat treatment, the homogeneity of the air bubbles can be maintained and the retention of the thickness of the films that are formed can be increased. At the same time, it is possible to stably produce foams with a high expansion ratio that contain a large amount of gas. Furthermore, the use of phosphates (I)-(III) in the concentration process after the production of a synthetic resin emulsion is useful in the stable production of synthetic resin emulsions with a high solids concentration, which is advantageous with regard to expansion molding (foaming).

Thus the use of a mixture of a polyurethane emulsion and/or a vinyl polymer emulsion as a base becomes possible, and the mechanical strength, heat resistance, cold resistance, light resistance, chemical resistance, and elasticity of the foams prepared using the process of the present invention are far superior to those prepared using conventional processes.

Examples of bubbling (or foaming) assistants which can be added to synthetic resin emulsions that contain phosphates (I)-(III) of the present invention include sodium laurate, coconut oil soap, sodium myristate, ammonium stearate, sodium oleate, higher alcohol sodium sulfate esters, higher fatty acid amide sodium alkylsulfonates, saponin, gelatin, or casein, etc. Fluor-

ine-containing surfactants that contain  $C_{1-20}$  perfluoroalkyl groups or fluoroalkyl groups can also be used.

For viscosity-adjusting agents, casein, alginate, gum arabic, bentonite, clay, carboxylated methylcellulose, poly(vinyl alcohol), poly(vinylpyrrolidone) copolymer, poly(oxyethylene oxide) polymer, poly(acrylic acid) emulsions, etc. can be used. The amount to use is suitably 0.1-5 parts, and preferably 0.5-3 parts. A suitable viscosity for the synthetic resin emulsions is 1,000-15,000 cp.

For crosslinking agents, water-soluble melamine-formaldehyde resin, water-soluble urea-formaldehyde resin, water-soluble or water-dispersible epoxy resin, aziridines, poly(isocyanate) resin, etc., can be used.

For sufficiently exhibiting the properties of foams with a polyurethane resin-like elasticity, the addition of a silicone oil is effective. Suitable examples of silicone oil include dimethylsilicone oil, methylphenylsilicone oil, amino-modified silicone oil, polyether-modified silicone oil, etc. The amount to be added is 0.1-3 parts by weight per 100 parts by weight of the emulsion. A silicone oil that has been emulsified in advance can also be used.

Coloring agents, fillers, antioxidants, antifungal agents, etc., can also be used as long as they do not impair the object of the present invention.

Thus a synthetic resin emulsion that contains (I)-(III) whose (emulsion) viscosity has been suitably adjusted is formed using a known process in rubber latex, then converted to a synthetic resin emulsion with uniform fine bubbles. In this case, foaming is generally done mechanically, however, there are no limitations with regard to the foaming machine to be used. For example, a machine which is generally used for the foaming of rubber latex can be used. An actual example is as follows: A synthetic resin emulsion containing random copolymer(s), whose viscosity is adjusted to a suitable value, and if necessary to which a foaming assistant, a viscosity-adjusting agent, a foam control agent, a crosslinking agent, etc., have been added, is transferred to a foaming machine by a gear pump, etc. A gas (usually air) is then fed into the foaming machine using a compressor. The flow rates are controlled by gauges. The emulsion which is fed into the foaming machine is mixed there with the gas, and by the action of the rotating cylinder, the gas being fed in is more finely dispersed in the synthetic resin emulsion. The synthetic resin emulsion foamed in this way then leaves the foaming machine. The amount of admixed gas (ratio of the gas to the synthetic resin emulsion), which relates to the density of the foamy substance of the synthetic resin emulsion after drying, can be controlled by controlling the amount of gas fed in, and the size of the bubbles can be controlled by the viscosity of the synthetic resin emulsion and the rotational speed of the cylinder. A hand mixer

is sufficient for foaming the synthetic resin emulsion on an experimental basis. In this case, the expansion ratio is generally 1.5- to 6-fold.

The synthetic resin emulsion foamed in this way is poured into a mold or spread on a substrate and then dried. A doctor blade is generally used for coating the emulsion on a substrate to a uniform thickness. Examples of suitable substrates include fiber products such as woven fabrics, knitted fabrics, raised variants of these fabrics, flocked fabrics, nonwoven fabrics, etc.; films with releasability such as paper, poly(vinyl chloride) sheet, leather sheet, release paper, polypropylene, polyester, glass plate; metal plate, etc.

By drying the coated synthetic resin emulsion that contains bubbles, the dispersion medium (water) can be removed to obtain a bubble-like substance that contains fine, uniform bubbles. The drying temperature is suitably 60-160°C, and preferably 100-140°C. When the emulsion can be cured by a heat treatment, the heat treatment is carried out after the drying process.

#### Effect of the Invention

According to the process of the present invention, the bubbles of synthetic resin emulsion are stable, therefore they can be easily applied to various substrates, and the foams obtained in this way can be used for various purposes such as bags, clothing, shoes, briefcases, etc., which are made of synthetic leather or artificial leather. Other uses include pseudo-leather coated fabric, carpet (backing), foot warmer (quilted) mats, doormats, bathroom mats, sponge sheets, or other articles and foams. And there are additional uses as well, e.g., while a foam is being formed it can also be used as an adhesive layer, and after a foam is formed, it can be subjected to an embossing process. For example, a foam layer is formed between a substrate (I) and substrate (II) and the two substrates are affixed simultaneously, or a foam is formed on one substrate, and at the same time the substrate and another compact substrate are affixed, and there can be a flocked foam in which the foam also serves as the binder of a pile. And the foams that are formed can be subjected to post-embossing to form a secondary uneven pattern. This is a good example of the excellent adhesion of the cell walls under fixed heat/pressure, which is another characteristic of the foams of the present invention. Still another characteristic is that of residual high elasticity with a high expansion ratio.

Examples of the above-mentioned uses and directions for use are not limited to those mentioned above, which are just examples that take advantage of the foamability characteristics of the present invention, which are very useful on an industrial basis.

Examples will now be presented to better explain the present invention. "Parts" and "%" as used in the examples refer to "parts by weight" and "% by weight", respectively, unless otherwise specified.

Reference Example 1

500 parts of polyoxypropylene glycol (average molecular weight 1,000) and 175 parts of tolylene diisocyanate were mixed and reacted at 80°C for 2 hours to prepare a prepolymer with 712 equivalents of NCO, then 270 parts of toluene was added to form a homogeneous solution. Next, 140 parts of the prepolymer solution was fed into a mixer which rotated at 12,000 rpm, 70 parts of an aqueous solution containing 6 parts of polyoxyethylene nonylphenyl ether with 25 moles of added ethylene oxide was added to the mixer, and then the resulting mixture was stirred for 3 minutes. Next, while the emulsion obtained in this way was being slowly stirred, an aqueous chain extender solution prepared by dissolving 8.2 parts of 1,6-hexamethylenediamine in 30 parts of water was added dropwise in a period of 2 minutes. When the addition was complete, the mixture was stirred slowly and continuously for 2 hours to obtain a stable polyurethane emulsion (A-1). The solids content was 46% and the viscosity was 850 centipoise.

Next, 1.0 part of sodium hexametaphosphate was added to the polyurethane emulsion (A-1) and concentration was carried out to obtain a polyurethane emulsion (A-2) with a solids content and viscosity of 55% and 900 cps, respectively.

Reference Example 2

110 parts of deionized water, 1.0 part (as solid matter) of Lacstar DS-801 (Dainippon Ink and Chemicals, Inc.), 1.0 part of biphenyl ether sodium sulfonate (Newcol 271A, Nippon Nyukazai Co., Ltd.), 0.5 part of tertiary dodecyl mercaptan, and 0.1 part of ammonium ethylenediaminetetraacetate were put in an autoclave equipped with a stirrer (the air inside the autoclave was replaced with nitrogen gas). Next, 100 parts of a monomer composition (60 parts of butadiene, 35 parts of methyl methacrylate, and 5 parts of itaconic acid) and 0.5 part of potassium persulfate were added. Then, while the resulting mixture was being stirred, emulsion polymerization was carried out at 60°C until 99.0% of the monomer mixture was polymerized. A 10% potassium hydroxide solution containing 1.0 part of sodium hexametaphosphate and 0.5 part of sodium tripolyphosphate was then added to the aqueous dispersion of the polymer after completion of the polymerization to carry out the concentration removal of unreacted monomers by steam distillation to obtain a

methyl methacrylate-butadiene copolymer emulsion (B-1) with a solids content, viscosity, and pH of 55.0%, 100 cps, and 8.9, respectively.

An aqueous dispersion of the polymer (B-2), with a solids content, viscosity, and pH of 55.0%, 4,500 cps, and 8.7, respectively, was prepared in the same way, except for the omission of sodium hexametaphosphate and sodium tripolyphosphate.

#### Actual Example 1

An aqueous solution of carboxymethyl cellulose was added to a mixed emulsion consisting of 50 parts of polyurethane emulsion (A-1) and 50 parts of methyl methacrylate-butadiene copolymer emulsion (B-1) containing sodium hexametaphosphate and sodium tripolyphosphate to adjust the viscosity to 8,000 centipoise, then 1 part of silicone oil, 3 parts of glycerol triglycidyl ether, and 4 parts of ammonium stearate were added and homogeneously mixed together.

The resulting mixture was foamed using a continuous mechanical foaming machine (Suga Kikai Co., Ltd.), then it was coated on cotton broadcloth and heated at 120°C for 8 minutes to obtain a foam sheet with a smooth surface and uniform fine bubbles. The abrasion resistance and light resistance of the foam sheet were excellent. Table 1 lists the physical properties of the foam sheet prepared in this way.

#### Comparison Example 1

The same procedure as in Actual Example 1 was carried out except that methyl methacrylate-butadiene copolymer emulsion (B-2) containing no sodium hexametaphosphate and sodium tripolyphosphate was used instead of using a methyl methacrylate-butadiene copolymer emulsion (B-1) that contained sodium hexametaphosphate and sodium tripolyphosphate. Table 1 lists the physical properties of the foam sheet prepared in this way.

#### Actual Example 2

The same procedure as in Actual Example 1 was carried out except that a polyurethane emulsion (A-2) containing sodium hexametaphosphate was used instead of using polyurethane emulsion (A-1). Table 1 lists the physical properties of the foam sheet prepared in this way.

#### Actual Example 3

The same procedure as in Actual Example 2 was carried out except that a methyl methacrylate-butadiene copolymer emulsion (B-2) containing no sodium hexametaphosphate and sodium tripolyphosphate was used instead of using a methyl methacrylate-butadiene copolymer emulsion (B-1) that contained sodium hexametaphosphate and sodium tripolyphosphate. Table 1 lists the physical properties of the foam sheet prepared in this way.

Reference Example 3

120 parts of deionized water and 0.3 part of a sodium alkylbenzenesulfonate (Neopelex F-25, Kao Corporation) were put in a stainless steel reactor, 0.4 part of ammonium persulfate and 0.2 part of sodium bicarbonate were added and dissolved in the reactor, then the temperature was raised to 75-80°C in a nitrogen stream. Next, 10 parts of a monomer emulsion prepared by emulsifying 55 parts of ethyl acrylate, 25 parts of butyl acrylate, 14 parts of methyl methacrylate, 4 parts of itaconic acid, and 2 parts of **N**-methylol methacrylamide with 0.3 part of a sodium alkylbenzenesulfonate (Neopelex F-25, Kao Corporation) in 30 parts of water was put in the reactor and polymerization was carried out. After 30 minutes, the remaining monomer emulsion was added dropwise at the same temperature over a period of 180 minutes, and after copolymerization, the contents were maintained at that condition for 30 minutes to complete the copolymerization. When the emulsion polymerization was completed, the solids content was 44.5%. Next, a solution prepared by dissolving 1.0 part of sodium pyrophosphate in water was added to the synthetic resin emulsion after completion of the emulsion polymerization and concentration was carried out to obtain a synthetic resin emulsion (C-1) with a solids content, viscosity, and pH of 55.0%, 250 cps, and 7.0, respectively.

Actual Example 4

The same procedure as in Actual Example 1 was carried out except that only 100 parts of methyl methacrylate-butadiene copolymer emulsion (B-1) containing sodium hexametaphosphate and sodium tripolyphosphate was used. Table 1 lists the physical properties of the foam prepared in this way.

Actual Example 5

The same procedure as in Actual Example 1 was carried out except that only 100 parts of urethane resin emulsion (A-2) containing sodium hexameta-phosphate was used. Table 1 lists the physical properties of the foam prepared in this way.

Actual Example 6

The same procedure as in Actual Example 1 was carried out except that acrylic copolymer emulsion (C-1) containing sodium pyrophosphate was used instead of using methylmethacrylate-butadiene copolymer emulsion (B-1) containing a sodium hexametaphosphate and sodium tripolyphosphate. Table 1 lists the physical properties of the foam prepared in this way.

TABLE 1. KEY: (a) example; (b) Actual Example . . . ; (c) Comparison Example 1; (d) synthetic resin emulsion; (e) urethane emulsion (a); (f) copolymer emulsion (b); (g) type of phosphate; (h) condition of the foaming solution; (i) condition of the foam; (j) physical properties of the foam; (k) abrasion resistance; (l) light resistance; (m) "a"; (n) "b"; (o) discoloration; and (p) none.

Notes:

- (1) the "a" in the Table indicates a 2-fold foaming solution (1-mm coating) and "b" indicates 5-fold foaming (expansion ratio) (5-mm coating).
- (2) The "condition of the foaming solution" was investigated by visibly comparing the bubble conditions when the mechanical foaming solution was placed in a 500-cc beaker with the bubble conditions when it was allowed to stand 5 minutes and then about 1 cm of the top layer was scraped off. "O" = the bubbles were fine and uniform and there was no change; "O" = the bubbles were fine and uniform, but their size increased; " $\Delta$ " = the bubbles were slightly nonuniform and their size increased considerably; and "x" = there were many large bubbles and the foaming solution was very nonuniform.
- (3) The "condition of the foam" was investigated by observing the bubble condition of a cross section of the foam and the smoothness of the surface. "O" = the bubbles were fine and uniform and the surface was smooth; "O" = there were rough bubbles and the surface smoothness was not quite as good; " $\Delta$ " = the bubbles were rough and there were some cracks; "x" = there were cracks.
- (4) The "abrasion resistance" was measured by a Gakushin-type abrasion tester (number of times to breakage under a 500 g load using the flat method).

(5) The "light resistance" was investigated by the degree of color change after abrasion resistance had been tested and after fade meter irradiation for 20 hours. The degree of color change is indicated as: "0" = no color change; "0" = slight yellowing; and "x" = extensive yellowing (turned yellowish brown).